

A BENT LAUE ANALYZER FOR X-RAY FLUORESCENCE SPECTROSCOPY

The new optic described in this report is capable of improving the sensitivity of x-ray fluorescence spectroscopy by eliminating the undesired photons *before* they reach the detector. The optics is an appropriately bent, thin silicon crystal, which is positioned to diffract the desired fluorescence x-rays. The Laue geometry is used in which the x-rays propagate through the crystal, and the undesired photons are eliminated by a system of slits. The merits and the limitations of the new approach are discussed.

X-ray absorption fine structure (XAFS) spectroscopy is a powerful tool for studying the molecular structure of solids, liquids, and molecular gases. Using XAFS allows the experimenter to “tune into” selected atomic species in complex materials and precisely determine average distances to nearby atoms, to identify what and how many nearby atoms there are, and related information. In many cases, XAFS also can provide information about local site symmetry and the oxidation state of the selected species. Often the experimenter can tune into different types of atoms to get a more complete picture of the sample as a whole.

A significant strength of XAFS is that, unlike x-ray diffraction, it can be applied to amorphous materials and solutions. Also, it does not require special sample conditions, so that it is possible to study a wide variety of materials under conditions similar to their natural states. It is possible to vary the sample conditions, such as temperature, pressure, pH, oxidation/reduction potential, and electric and magnetic fields, and then study the changes in local structure that are induced by those conditions. Systematic comparison between the functional behavior and the structures of metalloproteins by site-directed mutagenesis is of great value. Analogous systematic studies of the properties of materials and catalysts are similarly beneficial. These characteristics make XAFS a powerful tool for studies in physics, chemistry, biology,

materials science, geosciences, environmental science, and a wide array of engineering disciplines.

For dilute systems in which the atomic species of interest is a small proportion of the total number of atoms, XAFS requires intense x-ray beams. When the concentration becomes less than several hundred parts per million, it becomes preferable to measure the x-ray absorption coefficient indirectly by detecting the characteristic fluorescence x-rays that are emitted by the element of interest. These emerge radially from the sample in all directions and are accompanied by fluorescence x-rays from other elements in the sample, and x-rays that are scattered. The goal is then to efficiently collect those x-rays, and then to select and count the particular fluorescence x-ray photons of interest.

Conventionally, the fluorescence is often analyzed using commercial solid-state detector arrays, which count each fluorescence photon and determine its energy through electronic means by measuring the number of electron-hole pairs created in semiconductors (silicon or germanium). Although these detectors are suitable for many purposes, they have serious limitations: count rate, energy resolution, and cost. The count rates per channel are in the several hundred kilohertz range, the energy resolution is generally greater than 150 eV, and presently the costs are several hundred thousand dollars including electronics.

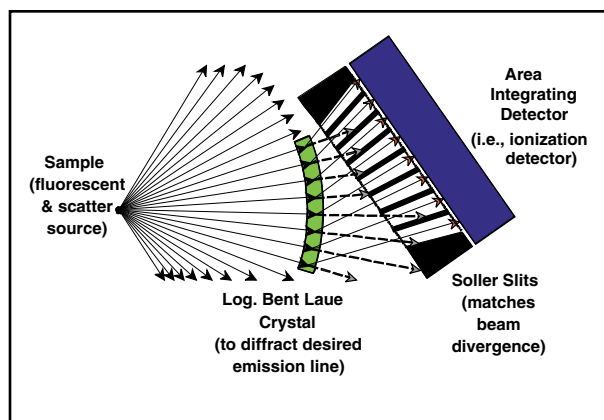


FIG. 1. A sketch of the "logarithmic bent Laue analyzer" concept.

Many samples of interest in materials science and environmental science are composed of a wide variety of elements, and sometimes the resolution of the solid-state detector arrays are insufficient to separate the fluorescence lines from different species. Furthermore, the x-ray fluxes delivered in the full beam from undulator beamlines at the Advanced Photon Source (APS) are very intense, and the undesired x-rays scattered off the sample can quickly saturate conventional photon-counting detectors. These costly detectors become overloaded by photons you never wanted in the first place. There had to be a better way.

For these reasons, we have tried different approaches for eliminating the undesired photons *before* they reach the detector. Initially, a device based on arrays of synthetic multilayers was developed by Zhang, Rosenbaum, and Bunker [1], and it has been successfully used for several years on the Bio-CAT (sector 18) beamline at the APS. However, the performance of this instrument is marginal at x-ray energies exceeding 15 keV, and another solution was needed. In 1995, Bunker, Chapman, and Zhong tried a new approach [2] based on an optic developed for medical imaging by Zhong, Chapman, and collaborators [3,4]. This concept was presented in 1998 at the International XAFS Conference in Chicago and has been further devel-

oped since then. The initial test results were presented at the SRI'99 Conference in Stanford, California [5].

The basic idea is simple but surprisingly effective: An appropriately bent thin silicon crystal is positioned so as to diffract the desired fluorescence x-rays. The Laue (hence the name) geometry is used, in which the x-rays propagate through the crystal. The diffracted beam is deflected by twice the Bragg angle (typically 10° - 20°) through slits that are aligned parallel to the diffracted beams, so they are not blocked. The desired photons are then collected by an inexpensive large-area-integrating detector, such as an ionization chamber. Conversely, the scattered x-rays and fluorescence from other elements in the sample produce photons at different energies, and these are not deflected; they travel straight through the crystal and are then blocked by the slits (Fig. 1). The slit material (Sn) is chosen so that the fluorescence from the slits (induced by the absorbed x-rays) is of sufficiently low energy that it is absorbed by air and the detector windows.

In order for the whole crystal to diffract, the x-rays incident on each part of the crystal must hit the crystal at the correct (Bragg) angle, which means the crystal needs to be bent to a specific logarithmic spiral shape (or sufficiently good approximation). Logarithmic spiral shapes are commonly found in nature, for example in Nautilus shells and flowers, because this mathematical shape derives from a simple growth rule: grow radially outward by an

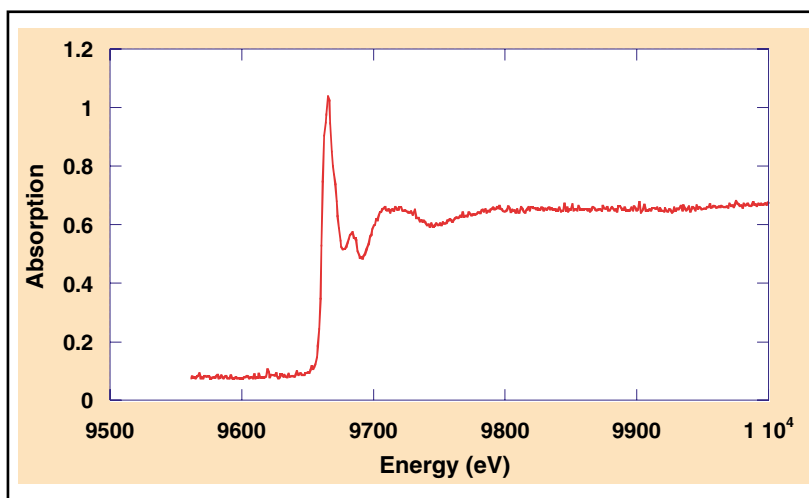


FIG. 2. An XAFS spectrum of around 65 ppm Zn - adsorbed to montmorillonite clay - measured with Logarithmic Bent Laue Analyzer.

amount in proportion to the present size, turn through a specific angle, repeat.

The surprising thing about this approach is that bending the crystals a sufficiently large amount dramatically changes the diffraction properties, in effect making the near-perfect crystals, which are exquisitely sensitive to alignment, act like highly imperfect crystals that are roughly 20 times more forgiving. This greatly improves detection efficiency and enormously simplifies construction of the devices (and hence the cost) and experimental alignment. We have found that very simple numerically machined crystal bending forms can be fabricated to sufficient accuracy, at very reasonable cost. Although the concept was originally intended for use at higher energies it is also well suited for much lower energies, even potentially as low as 4 keV. A representative XAFS spectrum of around 65 ppm Zn absorbed to Montmorillonite clay is shown in Fig. 2.

One attractive characteristic of this device is that, by choosing the optimal designs for a particular application, the performance can be optimized with respect to various characteristics such as energy bandwidth, optimal x-ray beam spot size, and throughput.

There are some limitations. These devices typically require beams that are limited in size to approximately 100 μm in one direction (usually vertical) and a millimeter or so in the other direction, so that focusing optics on the beamline are beneficial, though not absolutely required. This characteristic makes the bent Laue analyzer a particularly good match for the characteristics of third-generation synchrotron sources, and the small energy bandwidth (~ 10 eV) makes it a uniquely suitable choice for microfocusing beamlines.

Bent Laue optic is versatile and can serve as the basis for innovative and useful devices in synchrotron radiation research. We are developing cost effective approaches for optimization and manufacture so that experimenters can take advantage of this simple and useful new technology.

Bio-CAT is supported by the National Institutes of Health RR08630, additional support was provided by the U.S. Department of Energy (DOE), and the State of Illinois Higher Education Cooperative Agreement. The MR-CAT is funded by the member institutions and the DOE, Office of Science, Office of Basic Energy Sciences (BES), under Contract No. DE-FG02-94ER45525. Use of the Advanced Photon Source was supported by the DOE-BES, under Contract No. W-31-109-ENG-38.

Principal publication: "A Bent Laue Analyzer Detection System for Dilute Fluorescence XAFS," *Synchrotron Radiation Instrumentation, Eleventh U.S. National Conference*, edited by P. Pianetta et al., Vol. **521**, pp. 178-182 (American Institute of Physics, 2000).

REFERENCES

- [1] K. Zhang G. Rosenbaum, and G.J. Bunker, *Synchrotron Rad.* **6**, 220-221 (1999).
- [2] Z. Zhong, D. Chapman, B.A. Bunker, G.B. Bunker, R. Fischetti, and C.U. Segre, *J. Synchrotron Rad.* **6**, 212-214 (1999).
- [3] Z. Zhong, D. Chapman, R. Menk, J. Richardson, S. Theophanis, and W. Thomlinson, *Phys. Med. Bio.* **42**, 1751-1762 (1997).
- [4] P. Suortti, W. Thomlinson, D. Chapman, N. Gmur, R. Greene, and N. Lazarz, *Nucl. Instrum. Methods A* **297**, 268-274 (1990).
- [5] C. Karanfil, Z. Zhong, L.D. Chapman, R. Fischetti, G.B. Bunker, C.U. Segre, and B.A. Bunker, *Synchrotron Radiation Instrumentation, Eleventh U.S. National Conference*, edited by P. Pianetta et al., Vol. **521**, pp. 178-182 (American Institute of Physics 2000).

C. Karanfil,¹ L. D. Chapman,¹ G. B. Bunker,¹ Z. Zhong,² R. Fischetti,¹ C. U. Segre,¹ B. A. Bunker³

¹ *Physics Division and CSRRI, Illinois Institute of Technology, Chicago, IL, U.S.A.*

² *National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY, U.S.A.*

³ *Physics Department, University of Notre Dame, South Bend, IN, U.S.A.*